

CONVERSION OF WASTE POLYMERS TO ENERGY PRODUCTS

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ABSTRACT

A project was performed to determine the feasibility of converting waste polymers into diesel fuel. The primary waste polymer source of interest was disposable diapers, consisting of a mixture of cellulosic and synthetic polymer material in the presence of biological wastes. The overall project consisted of five phases: (1) reaction equilibrium calculations, (2) batch pyrolysis study, (3) continuous pyrolysis study, (4) continuous liquefaction study, and (5) integrated system demonstration. The integrated system consists of a circulating solid fluidized bed pyrolysis system to produce a synthesis gas for a fluidized bed catalytic liquefaction reactor. The objective for the pyrolysis system is to optimize the composition of hydrogen, carbon monoxide and ethylene in the synthesis gas for conversion to diesel fuel in the catalytic liquefaction reactor. The liquefaction reactor produces a product very similar to commercial No. 2 diesel fuel.

INTRODUCTION

Approximately 18% by volume of municipal solid waste consists of waste plastics (1). The 15.8 billion disposable diapers used annually comprise about 2% of the total waste stream. Due to increasing landfill costs and environmental and regulatory pressure, a flurry of activity has emerged to seek alternatives to landfill disposal of these materials. Proctor & Gamble, for example, has announced an "accelerated composting" program for their disposable diaper products (2). Separation steps are implemented to segregate the non-compostable parts from the cellulosic parts. The intent is to convert the cellulosic parts into "soil enhancer" (compost). Presumably, the plastics part still goes to the landfill. The questions would be the market for the "soil enhancer" and the probable necessity to still landfill the plastics. An alternative approach would be to convert the bulk diaper (all components) into marketable products with minimal landfill requirements. This approach has been developed at Arizona State University (ASU) utilizing over 100 different feedstocks, generally falling into the categories

of industrial wastes, municipal wastes, hazardous wastes and various agricultural and forest residues. An indirect liquefaction approach is used, i.e., gasification of the feed material to a gas followed by liquefaction of the gas to a No. 2 diesel grade transportation fuel. The sequence is illustrated in Figure 1. The objective in the gasification step is to maximize the production of hydrogen, carbon monoxide and ethylene while the objective in the second step is to maximize the production of diesel fuel from these three reactants. A high octane product can be produced via conventional catalytic reforming of the diesel material. The potential products are thus liquid hydrocarbon fuels, medium quality gas (ca. 500 BTU/SCF) and/or electricity (via heat recovery or combustion of the fuels). Alternative operating conditions and catalysts for the second stage reactor could produce other products (e.g., alcohols, methane etc.).

Prior work on this process has been described elsewhere (see, for example, references 3-6). This paper will present the application for disposable diapers. A five phase approach was used (reaction equilibrium calculations, batch pyrolysis study, continuous pyrolysis study, continuous liquefaction study, integrated system demonstration) with performance limited to an 11 month period. The intent was to minimize the project risks and costs for scale-up to a commercial configuration. Using the composition of a particular disposable diaper product ("Huggies") as an example, the maximum yields of diesel fuel (wet and dry basis) are illustrated in Figure 2. Realistic actual liquid product yields are expected to be in the 50-100 gals/ton range (dry basis).

EQUILIBRIUM CALCULATIONS

Composition analysis for three commercial disposable diaper products is shown in Table 1. Since the compositions are similar, Huggies will be used for example calculations. Assuming a gas product slate of hydrogen, carbon monoxide, ethylene, ethane, acetylene, methane and carbon dioxide, the equilibrium product composition was calculated as a function of temperature by minimizing the Gibb's free energy of formation subject to atom balance constraints. Results are shown in Figure 3. As shown, all components decrease with temperature except hydrogen and carbon monoxide. The desired hydrogen/carbon monoxide ratio of ca. 1.2 (based on prior work) is achieved at ca. 1100 K (1550 F). No ethylene is predicted at equilibrium, as expected in the presence of hydrogen.

BATCH PYROLYSIS STUDY

These experiments were performed in a Chemical Data Systems Model 122 Pyroprobe coupled to a Carle Gas Chromatograph Model AGC111H. The

Pyroprobe consists of a temperature programmed ampule containing a sample of the desired feedstock with product gas being swept to the gas chromatograph via helium carrier gas. A full factorial designed experiment was performed for the factors temperature and water composition. The experimental design is given in Figure 4 with the results shown in Table 2 using Huggies as the example feedstock. The base condition for temperature was set by results from the reaction equilibrium calculations. The three responses of interest are: (1) hydrogen + ethylene + carbon monoxide, (2) hydrogen/carbon monoxide, and (3) ethylene. The superior level for all three responses is at the high level for each factor (experiment E). The factor ranking (via analysis of variance calculations) and experimental error (as calculated by base point replication range divided by factorial experiment range) is shown in Table 3. All response results are considered to be favorable for further investigation in a continuous system.

CONTINUOUS PYROLYSIS STUDY

This task was performed in a reactor constructed from 3 inch schedule 40 pipe with a length of 3 feet. A fluidized bed configuration was utilized with electrical heating, a screw type solids feeder, overhead scrubber and recycle gas system via a compressor. Thus this phase was to be continuous with respect to feed and product withdrawal but batch with respect to the fluidized solid. Operating conditions for an experiment to study temperature effect on gas composition using a Huggies sample are shown in Table 4. The "steady state" conditions reported were determined by relatively stable periods of reactor temperature. Some problems were encountered in achieving consistent feed rates in this task. Gas composition results are shown in Table 5. The gas phase results are considered reasonable and favorable for liquid fuels production.

CONTINUOUS LIQUEFACTION STUDY,

A 2 inch fluidized bed reactor was used for this study (continuous gas feed, electrical heaters, cooling coils, continuous product withdrawal via a condenser and trap, catalytic noncirculating fluidized solid). The factors temperature, pressure and residence time were studied with regard to the responses of liquid product yields, bulk properties and yields. Gas feed was from cylinders based on the compositions achieved from the batch and continuous pyrolysis studies. A cobalt/alumina catalyst was used. Yields in the 20-30 gals/ton range were achieved in limited experimentation. These yields would be expected to improve substantially by implementing the following: (1) recycle of the off gas, (2) feed gas composition improvement, (3) catalyst improvement, and (4) liquefaction reactor optimization. Product quality information is provided in Table 6 as compared with commercial

materials. In general, this comparison indicates that the liquid fuel is a competitive product without any additional refining steps.

INTEGRATED SYSTEM DEMONSTRATION

This task was performed in an existing integrated system (Figure 5) consisting of a circulating solid fluidized bed gasification system followed by a fluidized bed catalytic liquefaction reactor. The intent was to run the system for an extended period of time at fixed operating conditions as determined by the previous tasks in order to report commercially realistic mass and energy balances for economic and scale-up studies. Unfortunately, this effort was hampered by lack of availability of a suitable solids feeder within the budgeted performance period. The problem is considered to be readily solvable with proper effort. Gasification composition data for a relatively stable period is shown in Figure 6.

SUMMARY AND CONCLUSIONS

The production of liquid hydrocarbon fuels from biologically contaminated disposable diapers is a technically viable concept. Favorable synthesis gas compositions can be produced. High quality liquid hydrocarbon fuel products can be produced from the synthesis gas. Additional research and development work is required to establish reliable mass and energy balances before scale-up is considered. To accomplish this objective, a reliable solids feeder system needs to be designed and tested. This is not considered to be a major obstacle.

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TABLE 1

Elemental Analysis of the Waste Polymer Samples.

COMPOUND	ELEMENT	SAMPLE 1 Huggies	SAMPLE 2 Lars	SOURCE (grams)
Cellulose	carbon	1.2	1.2397	1.4417
	hydrogen	1.09	1.1073	1.2668
	oxygen	0.81	0.8141	0.8141
Polystyrene	carbon	0.31	0.2561	0.1841
	hydrogen	1.06	0.9794	0.7173
	oxygen	0.13	0.2142	0.2037
SAC	carbon	0.167	0.2338	0.2216
	hydrogen	0.107	0.1623	0.125
	oxygen	0.01	0.0142	0.0142
Polychloride	carbon	0.2	0.2338	0.285
	hydrogen	0.4	0.6774	0.668
	chlorine	0.108	0.1635	0.2142
Epoxyresin	carbon	0.143	0.2145	0.4952
	hydrogen	0.143	0.2145	0.4952
	oxygen	0.016	0	0
Polyurethane	carbon	0.0516	0	0
	hydrogen	0.0516	0	0
	nitrogen	0.0014	0	0
Urethane	carbon	10.72	10.72	10.72
	nitrogen	2.38	2.38	2.38
	oxygen	0.5	0.5	0.5
TOTAL	carbon	2.2916	2.2674	2.1104
	hydrogen	12.6448	12.5118	12.425
	nitrogen	7.1101	7.1101	7.1101
TOTAL	carbon	0.011	0.0232	0
	hydrogen	0.011	0.0232	0.0297

Uncorrected for glass	1.4	1.4
Carbon	1.4	1.4
Hydrogen	0.31	0.231

Source: Kimberly-Clark Corporation.

TABLE 3

Analysis of Variance Calculation Results.

RESPONSE	FACTOR RANK	% ERROR
$H_2 + CO + C_2H_4$	Temperature, Water	9.6
H_2/CO	Temperature, Water	9.8
C_2H_4	Water, Temperature	0

TABLE 2

Gas Compositions from Huggies
(Factors: Temperature and Water Addition).

EXPERIMENT	A	B	C	D	E
OPERATING CONDITION					
COIL TEMPERATURE (°C)	1375	1469	1577	1575	1467
(°F)	2503	2691	2871	2857	2673
REACTION TEMPERATURE (°C)	1095	1176	1258	1104	1096
(°F)	1999	2135	2296	1999	1999
WATER ADDED (WT %)	64.3	0	0	64.3	78.2
(PARTS PER 100 PARTS)	0.14	0	0	0.14	0.14
WATER CONVERSION (MOLE %)					
H_2	26	29	14.5	25	22
CO_2	19	19	34	16	20
C_2H_4	7	5	5	7	6
C_2H_2	3	1	3	3	3
C_2H_6	0	0.2	0	0	0
CH_4	13	11	10.8	14	14
CO	20	34	30.7	23	23
H_2/CO RATIO	0.59	0.53	0.47	0.53	0.59

TABLE 4

Experimental Details

Reactor: material..... 316 stainless steel
 diameter..... 0.75 in. (1.9 cm)
 length..... 3 ft

Sample: Huggies & synthetic urine

Operating Conditions:
 Pressure..... 3 psig
 Flow rate..... 0.5 g/min
 Feed rate..... 0.75 g/min
 Solid type..... Alumina (80 mesh)
 Solid loading..... 0.028 in.
 Fluidizing gas..... Recycle pyrolysis gas

Factor: Temperature..... 1400°F, 1700°F

Reactant: Gas Composition

TABLE 5

Task 3: % gmole of Gas Product at "Steady" State

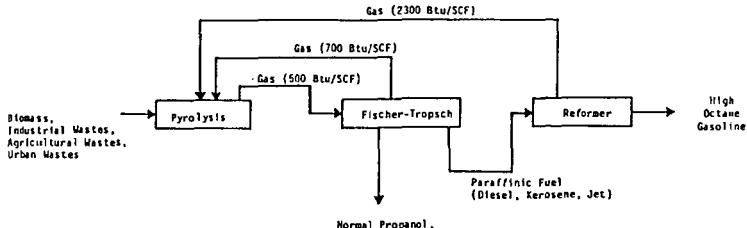
EXPERIMENT	A	B	C	D	E
Average Temperature (degree F)	1441.625	1532	1719.5	1658.5	1544
Range of time (min)	3.4	1.8	2.2	1.4	5
Hydrogen	34.05	34.71	56.72	48.74	39.54
Carbon dioxide	8.08	4.62	4.52	3.31	5.04
Ethylene	7.20	5.31	0.57	1.70	4.19
Ethane	1.27	0.97	0.20	0.22	1.28
Nitrogen	1.01	1.09	0.71	0.71	0.62
Methane	19.42	19.05	2.90	9.64	14.88
Carbon monoxide	27.97	34.25	34.81	55.68	34.08

TABLE 6

Properties of Fischer-Tropsch Product and Commercial Fuel Oils

	No. 2 Diesel	Kerosene	JP-4	Waste Polymers Feedstock
Specific Gravity	0.8360	0.8108	0.7988	0.7470
Gravity, API *	37.8	43	53	57.6
Boiling point range, °F				
10%	368	336	147	179
Evaporated at 50%	458	410	302	308
90%	563	478	438	826
Calculated cetane index	44.2	44.2	37.8	45.7
Heating value, BTU/lb.	19380	21978	22440	19056

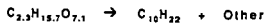
FIGURE 1



Basic Chemical Conversion Scheme

FIGURE 2

Huggies → Diesel



Composition (wt%)

	Huggies (wet)	Huggies (dry)	Diesel
C	17.54	53.44	84.51
H	9.97	7.64	15.49
O	71.82	37.19	0
N	0.02	0.04	0
Na	0.56	1.70	0

Maximum yield : 67 tons diesel
(carbon balance) ton Huggies (wet)

189 tons diesel
ton Huggies (dry)

FIGURE 3

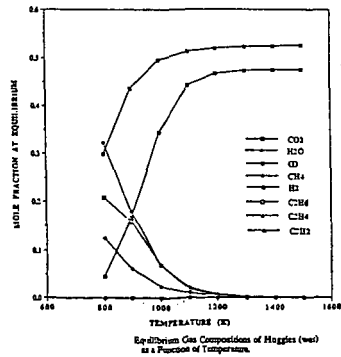


FIGURE 4

FACTOR	LEVEL		
	-1	0	+1
Temperature (K)	1019	1102	1185
Temperature (°F)	1375	1525	1675
Water (wt%)	0	64.3	78.3
(μ l/0.1 mg.)	0	0.18	0.36

PRESSURE: 1 atm
RESIDENCE TIME: 20 seconds

Experimental Design for Huggies.

FIGURE 5
CONVERSION SYSTEM SCHEMATIC

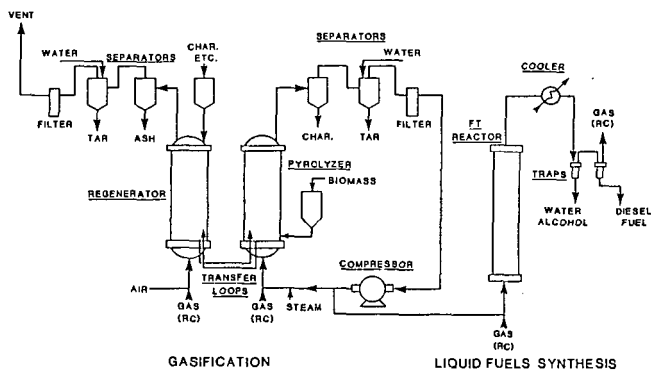


FIGURE 6

